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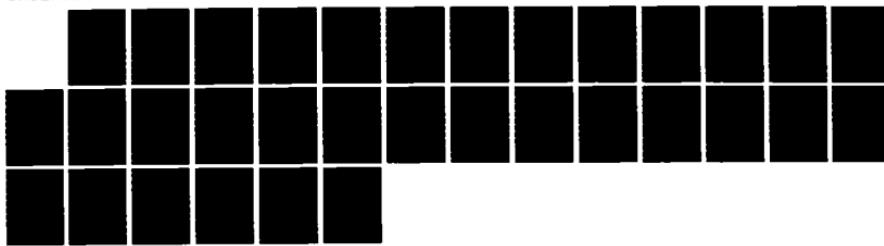
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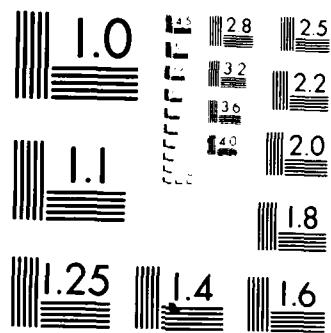
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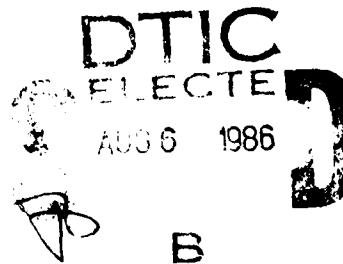
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"SOLUBLE ALKYL SUBSTITUTED
POLYGERMANES: THERMOCHROMIC BEHAVIOR"

by
R. D. Miller and R. Sooriyakumaran

Accepted for Publication in J. Polymer Science Chemistry Edition

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**SOLUBLE ALKYL SUBSTITUTED POLYGERMANES:
THERMOCHROMIC BEHAVIOR**

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ABSTRACT: We have prepared a number of high molecular weight, soluble, symmetrical dialkyl substituted germanium homopolymers and germanium-silicon copolymers. In solution, the absorption of the homopolymers was ~20 nm red shifted from the corresponding silicon derivatives. This was somewhat unexpected based on theoretical predictions and has been rationalized on the basis of conformational arguments. In the solid state, samples of poly(di-n-hexylgermane) and poly(di-n-octylgermane) are strongly thermochromic. The effect is attributed to the conformational locking of the backbone which is caused by the crystallization of the side groups. In this regard, the germanium derivatives behave similarly to the corresponding silicon polymers and the convergence of the long wavelength absorptions for both types of polymers is consistent with theoretical predictions. The germanium-silicon copolymers are also strongly thermochromic, but the long wavelength absorption is somewhat blue shifted (8 nm) from the respective homopolymers. As expected, the new germanium homo and copolymers are quite sensitive to light and readily undergo chain scission to produce lower molecular weight materials.

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INTRODUCTION

Although polymers containing only silicon in the backbone have been known for some time,^{1,2} the intractable nature of the early derivatives elicited little scientific interest until recently.³⁻⁵ Our interest in these materials was spurred by the demonstration that judicious choice of substituents could ultimately lead to soluble high polymers.⁵⁻⁸ It is now clear that polysilane high polymers represent a new class of radiation sensitive polymers for which a number of applications have been reported. Accordingly, they have been used as ceramic precursors,⁹ photoinitiators¹⁰ for vinyl polymerizations and most recently as exciting new materials for lithography.¹¹⁻¹³

Much of the scientific interest in catenated silicon polymers has centered around their very unusual electronic spectra.¹⁴⁻¹⁵ Although the backbone is composed entirely of sigma bonds, all high molecular weight polysilanes absorb strongly in the UV. An unusual feature of this transition is that both the λ_{max} and the $\epsilon/\text{Si} - \text{Si}$ increase rapidly with molecular weight at first but appear to approach a limiting value for high molecular weight materials.¹⁶ In addition, the position of this limiting absorption in solution is a function of the substituents. It occurs between 305-325 nm for alkyl substituted materials, but is strongly red shifted to 335-350 nm when aromatic substituents are directly attached to the silicon backbone.¹⁶ Very recently, we have demonstrated that the limiting values for the λ_{max} apply only to materials in solution or in the amorphous solid state. Films of materials which are symmetrically substituted with long chain alkyl groups undergo a curious spectral red shift of 55-65 nm upon standing.¹⁷ For poly(di-n-hexylsilane) (PDNHS) which we have studied extensively, this behavior is thermally reversible. Interestingly, films of polysilanes derivatives with C₄ and C₅ substituents do not show the strong red shift upon standing while the C₇ and C₈ materials behave as PDNHS.¹⁸

By virtue of its close proximity to silicon in the periodic table, the chemistry of germanium and its derivatives is often similar to the related silicon derivatives. Like silicon, germanium derivatives form cyclic and acyclic catenates and these materials have been investigated theoretically and experimentally.¹⁵ In spite of this, relatively few germanium polymers have been prepared and characterized.¹⁹⁻²² Recently, however, West and Trefonas have described the preparation of the first soluble, high molecular weight germanium homopolymer and some silicon-germanium copolymers from dibutyl germanium dichloride.²³ In light of the very unusual spectroscopic behavior of the symmetrically substituted dialkyl polysilanes both in the solid state¹⁷ and in solution,^{24,25} we were quite anxious to prepare the related germanium polymers to compare the spectral effects of the increased atomic size and bond length of the germanium derivatives with the related silicon polymers.

One drawback to the systematic investigation of substituted germanium polymers is the lack of a commercial source for a variety of substituted dihalides. In this regard, only di-n-butylgermanium dichloride and diphenylgermanium dichloride and dibromide are commercially available. This situation was exacerbated by the observation that, in our hands, the stoichiometric reaction of Grignard or lithium reagents with germanium tetrachloride failed to provide a useful preparative route to the desired symmetrical dialkyl germanium dihalides.²⁶ For this reason, two alternative routes to the desired germanium dihalides were utilized. Scheme I shows that both bromides and chlorides could be prepared from readily available diphenylgermanium dichloride.^{27,28} This procedure was somewhat cumbersome, however, for the preparation of dialkyldichlorogermanes on large scale. For this reason, a equilibration route shown in

Scheme II^{29,30} was utilized for the preparation of the new monomers on the scale needed for the polymerization studies.

EXPERIMENTAL

Dichlorodiphenylgermane and germanium tetrachloride were purchased from Alfa. The dihexyldichlorosilane used in the copolymerizations was purchased from Petrarch Systems Incorporated. All monomers were carefully fractionally distilled and determined to be better than 98% pure by glpc analysis (10% SE-30 on 60/80 Chromosorb W) before use. The solvents were routinely dried in solvent stills (toluene and octane over sodium, diglyme over lithium aluminum hydride) and distilled before use. The sodium used in the polymerization was purchased form Aldrich as a 40% dispersion in light mineral spirits. The exact concentration was determined prior to use by hydrolysis with isopropyl alcohol and measurement of the gas evolution. Poly(di-n-hexylgermane) 1 was prepared by the dehalogenation of either di-n-hexylgermanium dibromide or dichloride using sodium in toluene or in a toluene-diglyme mixture. For this polymer, a study of the effect of the order of reagent addition, *i.e.*, halide to sodium (normal) or sodium to halide (inverse) on the yield and molecular weight distribution was made. For the preparation of poly(di-n-butyl), poly(di-n-pentyl), and poly(di-n-octyl)germanes, the respective dialkyldichlorogermanes were utilized and the mode of sodium addition was normal. The copolymer poly(di-n-hexylgermane)-co-(di-n-hexylsilane) was prepared in a similar fashion using a 1:1 feed ratio of the respective monomers.

Dibromo Di-n-hexylgermane. Two molar equivalents of bromine in 1,2-dichloroethane (12.49g, 0.078 mole) were added dropwise over 0.5h to a solution of 15.0g (0.038 mole) of diphenyl-di-n-hexylgermane (prepared from the addition of excess n-hexyl magnesium bromide to diphenyl germanium dichloride) in 80 mL of 1,2-dichloroethane. The

reaction mixture was refluxed for 6h and the solvent removed on the rotary evaporator.

The residue was fractionally distilled through a 6" Vigreux column to yield

dibromo-di-n-hexylgermane: bp 120-130°C (0.1 mm); ^1H NMR $\delta(\text{CDCl}_3)$ 0.8(t,6H), 1.36(br m,2H), and 1.56(br m,4H)

Anal. Calcd. for $\text{C}_{12}\text{H}_{26}\text{Br}_2\text{Ge}$: C, 42.02; H, 7.76; Ge, 25.40. Found: C, 42.42; H, 7.79; Ge, 24.97.

Dichloro-Di-n-hexylgermane. Dibromo-di-n-hexylgermane (2.0g, 0.005 mole) was refluxed with 10 mL of 20% sodium hydroxide solution for 3h. The mixture was cooled and extracted with ether. The ether was washed with water and dried over Na_2SO_4 . The solvent was removed to yield 0.9g (70%) of the di-n-hexylgermanium oxide trimer. ^1H NMR $\delta(\text{CDCl}_3)$ 0.9(t,6H), 1.05(m,4H), and 1.33(br m, 16H); IR(neat) 2960, 2930, 2870, 2860, 1465, 1380, 1105, 1065, and 840 cm^{-1} ; mass spectroscopic analysis, no parent ion, 683($\text{M}^+-\text{C}_6\text{H}_{13}$), typical germanium isotopic cluster 683-699.³¹

Anal. Calcd. for $\text{C}_{36}\text{H}_{78}\text{Ge}_3\text{O}_3$: C, 41.88; H, 7.47; Ge, 15.82. Found: C, 41.79; H, 7.49; Ge, 15.39.

The crude product was heated with 10 mL of conc. HCl for 2h. The mixture was cooled and extracted with ether. The ether was dried over Na_2SO_4 and removed on the rotary evaporator. The product was fractionally distilled to yield dichloro-di-n-hexylgermane 1 in quantitative yield: bp 130-8°C (2.6 mm); ^1H NMR $\delta(\text{CDCl}_3)$ 0.85(t,6H), 1.30(br m, 16H), and 1.56(br m,4H);

Anal. Calcd. for $\text{C}_{12}\text{H}_{26}\text{Cl}_2\text{Ge}$: C, 45.92; H, 8.35; Ge, 23.13. Found: C, 45.55; H, 8.48; Ge, 22.75.

Preparation of Dichloro-Di-n-hexylgermane by Equilibration. Germanium tetrachloride (15.16g, 0.07 mole), tetra-n-hexylgermane (35g, 0.084 mole) and freshly sublimed aluminum chloride (1.9g, 0.014 mole) were mixed in a glass liner and placed in a Parr pressure bomb. The bomb was sealed and heated to 200°C for 5h. After cooling to 25°, the dark brown reaction mixture was diluted with 500 mL of hexane and filtered. The product was concentrated on the rotary evaporator and fractionally distilled through a 6" Vigreux column to yield 31.9g (70%) of dichloro-di-n-hexylgermane. This material had identical spectral and chromatographic properties to that described above. The other dichloro-di-n-alkylgermanes were prepared in a similar fashion and were purified by distillation.

Dichloro-Di-n-pentylgermane: bp 94°C (0.2 mm) ^1H NMR $\delta(\text{CDCl}_3)$ 0.86(t,6H), 1.36(br m, 12H), and 1.56(br m,4H); mass spectroscopic molecular weight, 282(M^+), 246(M^+-Cl), 246(M^+-HCl) 211($\text{M}^+-\text{C}_5\text{H}_{11}$) and 176($\text{M}^+-\text{C}_5\text{H}_{11}\text{Cl}$).

Anal. Calcd. for $\text{C}_{10}\text{H}_{22}\text{Cl}_2\text{Ge}$: C, 42.02; H, 7.76; Ge, 25.40. Found: C, 42.42; H, 7.79; Ge, 24.97.

Dichloro-Di-n-octylgermane: bp 135-140°C (0.15 mm) ^1H NMR $\delta(\text{CDCl}_3)$ 0.85(t,6H), 1.26(br m, 24H), and 1.56(br m,4H); mass spectroscopic molecular weight 366(M^+), 331(M^+-Cl), 330(M^+-HCl), 253($\text{M}^+-\text{C}_8\text{H}_{17}$), 218($\text{M}^+-\text{C}_8\text{H}_{17}\text{Cl}$).

Preparation of Poly(di-n-hexylgermane) 1. Into a dry 100 mL three necked flask equipped with a condenser, high speed overhead stirrer, argon inlet and addition funnel was placed the sodium dispersion (3.8g,(38.5%),0.064 mole) and 20 mL of dry toluene. Distilled dichloro-di-n-hexylgermane was added to the addition funnel and the flask was heated to 135°C in an oil bath. The monomer was then added to the stirred dispersion

over 10m. The reaction was quite exothermic and turned purple instantly. After the addition, the reaction was stirred at 135-145°C for 2h. The mixture was cooled to room temperature and 20 mL of isopropyl alcohol was continuously added to quench the reaction. The reaction mixture was then poured into 300 mL of isopropyl alcohol with strong stirring and the precipitate gravity filtered and air dried. The dried precipitate was dissolved in 200 mL of toluene at 60°C. After cooling, the toluene solution was washed copiously with water and dried over Na₂SO₄. The solvent was removed on the rotary evaporator and the residue dried at 80°C in a vacuum oven for 48h to yield 730 mg (9.5%) of a somewhat tacky white solid. The polymer was solvent fractionated by dissolving in toluene and precipitating at room temperature by stirring with an equal volume of isopropyl alcohol. A similar procedure was used for the preparation and purification of the other polymers and copolymers described in this paper, and the results are reported in Tables I and II. In each case, the crude polymers showed a polymodal molecular weight distribution from which the higher molecular weight fractions were easily separated by solvent precipitation. The molecular weights and distributions were determined by GPC analysis using a Waters Model 150C liquid/gel permeation chromatograph with a refractive index detector and ASI ultragel columns.

The ¹H NMR spectra were recorded using a EM-390 instrument and tetramethylsilane as an internal standard. The ¹³C spectra were measured in chloroform-d₁ on a Varian CFT-20 machine. All infrared spectra of the polymer films were obtained on an IBM IR-32 fourier transform machine. The solution and solid film UV-visible spectra were measured either on a Cary 14 or a Hewlett Packard 8450A spectrometer. Irradiation experiments on the solid films were performed at an Optical Associates Incorporated Model 78 exposure station using narrow bandpass (10 nm) filters. The exposure doses were measured using a OAI exposure meter with sensing heads

calibrated for specific wavelengths. The composition of the copolymers was determined by elemental analysis and less accurately by ^1H NMR analysis by integration of partially overlapping bands. The DSC and TGA analyses were measured using a Dupont 990 instrument.

Poly(di-n-hexylgermane) (PDNHG) 1 was isolated as a tacky white solid which is soluble in chloroform, toluene, hexane, and THF: ^1H NMR $\delta(\text{CDCl}_3)$ 0.85(t,6H,-CH₃), 1.25(br m,20H,-(CH₂)₅-); ^{13}C NMR $\delta(\text{CDCl}_3)$ 14.09(-CH₃), 17.8, 22.92, 28.70, 31.82, and 34.26; IR(neat) 2957(s), 2922(s), 2872(s), 2851(s), 1464(m), 1377(w), 1163(w), 1097(w), 1307(w), 1001(w), 951(w); 837(w) 729(w), 629(m), and 621(m) cm^{-1} ; UV(C₆H₁₂) λ_{max} 340 nm.

Anal. Calcd. for C₁₂H₂₆Ge: C, 59.12; H, 10.79; Ge, 29.88. Found: C, 58.97; H, 10.22; Ge, 29.63.

Poly(di-n-pentylgermane)(PDNPG) 2 was isolated as a white solid which is soluble in chloroform, toluene, hexane and THF: ^1H NMR $\delta(\text{CDCl}_3)$ 0.83(t,6H,-CH₃), 1.26(br m, 16H, -(CH₂)₄-); ^{13}C NMR $\delta(\text{CDCl}_3)$ 14.16 (-CH₃), 17.82, 22.50, 28.29, and 36.73; IR(film) 2955(s), 2920(s), 2849(s) 1464(m), 1377(w), 1163(w), 1089(w), 1026(w), 956(w) 912(w), 794(w), 744(w), and 671(m) cm^{-1} ; UV(C₆H₁₄) λ_{max} 339 nm.

Anal. Calcd. for C₁₀H₂₂Ge: C, 55.89; H, 10.32; Ge, 33.78. Found: C, 55.59; H, 10.03; Ge, 34.25.

Poly(di-n-octylgermane)(PDNOG) 3 was isolated as a sticky, colorless solid: ^1H NMR $\delta(\text{CDCl}_3)$ 0.83(t,6H,-CH₃), and 1.25(br m,28H,-(CH₂)₇-); ^{13}C NMR $\delta(\text{CDCl}_3)$ 14.1 (-CH₃), 17.57, 22.79, 28.76, 29.33, 29.74, 32.12 and 34.68; IR(film) 2957(s), 2922(s),

2853(s) 1468(m), 1379(w), 1157(w), 1107(w), 987(w), 906(w), 827(w), 721(w), 668(m), and 625(w) cm^{-1} ; UV(C_6H_{12}) λ_{max} 342 nm.

Anal. Calcd. for $\text{C}_{16}\text{H}_{34}\text{Ge}$: C, 64.26; H, 11.46; Ge, 24.28. Found: C, 64.58, H, 10.83; Ge, 23.57.

Poly(di-n hexylgermane)-co-(di-n-hexylsilane) 4a, prepared in toluene, was isolated as a white solid: ^1H NMR $\delta(\text{CDCl}_3)$ 0.90(t- CH_3 and - $\text{CH}_2\text{-Si}$) and 1.30(br m); ^{13}C NMR $\delta(\text{CDCl}_3)$ 14.12, 15.15, 17.61, 22.92, 27.65, 28.71, 31.91 and 34.84; IR(film) 2955(s), 2922(s), 2851(s), 1468(m), 1417(w), 1377(m), 1248(w), 1172(w), 1103(w), 1035(w), 1001(w), 943(w), 891(w), 839(w), 754(w), 729(m), 719(m), and 669(s); UV(C_6H_{12}) λ_{max} 322; Anal. Found: C, 69.13; H 12.44, Si, 12.74, Ge, 7.79.

Poly(di-n-hexylgermane)-co-(di-n-hexylsilane) 4b, prepared in toluene -30% diglyme, was isolated as a white solid: ^1H NMR $\delta(\text{CDCl}_3)$ 0.83(t,- CH_3 and - $\text{CH}_2\text{-Si}$), 1.30(br m); IR(film) 2957(s), 2922(s), 2872(s), 2851(s), 1466(m), 1415(w), 1377(w), 1298(w), 1250(w), 1169(w), 1099(w), 1037(w), 999(w), 953(w), 891(w), 839(w), 719(w), and 669(m) cm^{-1} ; UV(C_6H_{12}) λ_{max} 326 nm; Anal. Found: C, 66.14, H, 12.16; Si, 6.82; Ge, 12.75.

The thermal stability of the germanium homopolymers and the germanium-silicon copolymers mirrored that of their silicon counterparts. In this regard, the polymers described were stable to $>300^\circ\text{C}$ as determined by thermal gravimetric analysis.

RESULTS AND DISCUSSION

The reaction of germanium tetrachloride with two equivalents n-hexylmagnesium bromide gave a complex mixture of products and was unsuitable for the preparation of the amounts of materials needed for polymerization studies. Since tetrasubstituted germanes were easily prepared by the reaction of excess Grignard reagent with either dichlorodiphenylgermane or germanium tetrachloride, we utilized the routes described in Schemes I and II for the preparation of the starting monomers.

We first investigated the polymerization of dibromo-di-n-hexylgermane under a variety of reaction conditions and the results are shown in Table I. The polymers produced in this study showed narrow molecular weight dispersitivities but were relatively in low molecular weight and had poor film forming properties. This was true even for the inverse addition mode which normally gives lower overall yields of higher molecular weight polymers.³² Interestingly, the use of diglyme as a cosolvent, which greatly increased the yields in the polymerization of sterically hindered dialkyl dichlorosilanes,¹¹ was relatively ineffective in this regard for the germanium polymers.

In an effort to produce higher molecular weight materials, the corresponding dichlorodialkyl germanes were examined as starting materials for polymerization and the results of this study are shown in Table II. Using dichloro di-n-hexylgermane as a model monomer, a variety of different reaction conditions were examined. In most cases, the crude product as isolated showed a polymodal molecular weight distribution which contained some low molecular weight oligomers ($\bar{M}_w < 2000$). As was observed in the polymerization of the dibromide, the use of diglyme as a cosolvent did not significantly increase the yield of polymer and resulted in considerably lower molecular weights. Similarly, inverse addition did not improve the situation markedly and very little high

molecular weight material was isolated from this run (Table II, entry 2). Interestingly, the molecular weight distribution of each fraction was quite narrow and the high molecular weight material was easily separated by solvent precipitation. Since variation in the reaction solvent did not result in significantly improved polymer yields and the use of the inverse addition mode did not give higher molecular weights, the standard technique utilizing the normal addition mode in toluene was employed for the preparation of the other polymers. In each case, the crude products contained a significant portion of higher molecular weight material which was easily separated by solvent fractionation. The copolymers 4ab were prepared by polymerization in either toluene or toluene-diglyme (Table II, entries 7 and 8) maintaining a 1:1 feedstock ratio of the monomers. Elemental analyses suggested that the compositions of the two fractionated high molecular weight copolymers were significantly different. In this regard, the silicon/germanium ratio in 4a was 3.3/1 while that in 4b was ~1.4/1. In each case, the elemental composition of the crude products as isolated differed significantly from that observed in the fractionated high molecular weight samples. The elemental composition of the copolymer can also be roughly determined by ¹H NMR, since the methylene group bonded to silicon appears slightly upfield and is partly merged with the corresponding methyl signals of both the silicon and germanium monomer unit. This method, while providing a qualitative check on the elemental analyses, is inherently less accurate because it involves the integration of overlapping resonances. The peaks in the ¹³C spectrum of 4a at δ17.61 and 28.71 have been tentatively assigned to the α and β carbons attached to germanium. In this regard the chemical shifts of these carbons are very similar in both the germanium homopolymer and the copolymer.

It is interesting to note that although the lower molecular weight materials prepared from dibromo-di-n-hexylgermane (Table I) had relatively poor film forming properties,

spectroscopically in solution, they appeared quite similar to the high molecular weight samples prepared from dichloro-di-n-hexylgermane. In this regard, the ^{13}C and ^1H NMR spectra of the fractionated materials (Table I, entries 1 and 3) were identical to those of the high molecular weight sample isolated from the polymerization of dichloro-di-n-hexylgermane (Table II, entry 1). Similarly, the spectra of the low molecular weight materials prepared from either the chloride or the bromide (Table I, entry 1 and Table II, entry 3) were identical. The IR spectra as measured on thin films were also identical except that the peak widths were slightly larger for the higher molecular weight materials. The UV spectra of the samples were also similar in shape but the lower molecular weight materials absorbed at slightly shorter wavelengths (332 *versus* 340 nm), which is consistent with earlier observations made on related silicon polymers regarding the relationship of the λ_{\max} and molecular weight.¹⁶

As mentioned earlier, one of the most unusual features of polysilane derivatives is their remarkable electronic spectra. Not only is the UV-visible absorption dependent on molecular weight and on the substituents, but it also appears to depend on the conformation of the backbone. This latter feature has been evoked as an explanation of the curious thermochromic effects displayed by some polysilanes both in the solid state¹⁷ and also in solution.^{24,25} Paramount to the explanation of these effects is the suggestion that the all trans configuration of a catenated silicon unit will have both a lower ionization potential³³ and will absorb at longer wavelengths than one containing gauche links. In this regard, the gauche links may represent kinks or partial interrupts in the chain conjugation. Since recent calculations on silane oligomers have suggested that trans and gauche configurations are relatively close in energy,^{34,35} it is not surprising that unconstrained polysilanes in solution at room temperature or in the amorphous solid state contain a distribution of trans and gauche conformations. We have suggested that the

unusual thermochromic behavior exhibited by films of poly(di-n-hexylsilane) is due to the conformational locking of the polymer backbone³⁶ enforced by side chain crystallization. This phenomenon was determined to depend critically on the nature and length of the alkyl substituent.¹⁸

Since earlier theoretical studies on group IV catenates have suggested that the electronic behavior of germanium catenates should be very similar to their silicon counterparts,¹⁵ we were anxious to compare the electronic absorption spectra of our germanium polymers both in solution and in the solid state.

West and co-workers have recently reported that unfractionated samples of poly(di-n-butylgermane)²³ have an absorption maximum at 333 nm in solution which is approximately 19 nm red shifted from its silicon counterpart. Although this was somewhat unexpected based on the observation that the absorption spectra of short chain germanium and silicon catenates are very similar,¹⁵ this shift was tentatively attributed to changes in the equilibrium backbone conformation of the germanium polymer relative to its silicon counterpart. This conformational redistribution is not unexpected considering the difference in the size of germanium relative to silicon and the longer bond length of the germanium-germanium bond. Now we report that fractionated high molecular weight samples of poly(di-n-butylgermane), poly(di-n-pentylgermane) 2, poly(di-n-hexylgermane) 1 and poly(di-n-octylgermane) 3 all absorb around 339-342 nm in solution. Since the molecular weights of these samples were all greater than 300,000, it is expected that these measured values have reached their limiting values. The copolymers poly(di-n-hexylgermane)-co-(di-n-hexylsilane) 4a (ratio 1:4.2) and 4b (ratio 1:1.4) absorbed at 322 and 326 nm, respectively. While these values are longer than the respective polysilane homopolymer (316 nm), they are considerably shorter

than the polygermane homopolymer 1 (340 nm). The shape of the copolymer band is symmetrical and does not appear to be significantly broadened. Figure 1 shows a comparison of the absorption spectrum of 4b with that of a 1:1 mixture of the two homopolymers poly(di-n-hexylsilane) ($\bar{M}_w = 1.6 \times 10^6$) and poly(di-n-hexylgermane) ($\bar{M}_w = 9.7 \times 10^5$). In the blend, a strong shoulder is clearly visible at ~340 nm which is apparently the contribution from 1. The absorption spectrum of the copolymer does not show any evidence of a shoulder at longer wavelengths nor is it unusually broad. This would seem to suggest that the copolymer appears more or less random and does not contain any *very* long blocks of the germanium polymer.

The absorption spectra of the germane homopolymers and germanium-silicon copolymers were also examined in the solid state as a function of temperature in order to answer the question of whether these materials are thermochromic like the related silicon polymers.

Thin films of PDNHG 1 were spun from a 2% isoctane solution into quartz or sodium chloride disks and the samples heated to 100° briefly to remove the residual casting solvent. The spectrum of the sample as cast showed a single featureless broad absorption with a maximum at 337 nm. This spectrum did not change upon standing at room temperature for two days nor was it altered when the sample was held under vacuum for 24h. This behavior was distinctly different from that observed in the case of poly(di-n-hexylsilane) (PDNHS) which crystallized rapidly upon standing at room temperature as manifested by the decrease in the original absorption at 316 nm and the appearance of a sharper peak at ~370 nm.¹⁷ This behavior was reversible upon heating above the melting transition at 41°C. DSC examination of PDNHG 1 showed a strong, broad endotherm which peaked at 12.4°C (see Figure 2). Upon cooling the heated

sample slowly, a strong crystallization exotherm was observed at -1°C . This thermal behavior was completely reversible and no other thermal transition was observed up to $\sim 200^{\circ}\text{C}$. When the sample was placed in a cryostat and cooled rapidly to -12°C , the broad absorption at 337 nm greatly decreased in intensity and was replaced by a sharper absorption at 370 nm (Figure 3). Allowing the sample to warm to room temperature resulted in the disappearance of the absorption at 370 nm and the reappearance of the broad band at 337 nm. The spectrum of the sample after warmup was not completely identical to the original since it retained a small peak at 354 nm which appeared on the tail of the original absorption. This peak disappeared upon heating and recooling. The observed spectral changes as a function of temperature were reversible. The spectral and thermal behavior of PDNHG 1 thus mimics that recently reported for poly(di-n-hexylsilane) for which we have suggested that side chain crystallization locks the polymer backbone into a regular configuration which is responsible for the spectral shift.¹⁷ It seems reasonable to propose a similar explanation for the thermochromic behavior of PDNHG, 1. In this regard, it would not be surprising that the increased atomic size of germanium relative to silicon and the longer Ge-Ge bond lengths effect the side chain melting transition. The observation that silicon and germanium high polymers have similar absorption spectra is in accord with theoretical predictions for infinite silicon and germanium catenates.¹⁵

In a similar fashion, poly(di-n-octyl)germane 3 shows thermochromic behavior. At temperatures below -20°C , the broad polygermane absorption at 340 nm was replaced by a sharper red shifted band at 369 nm. This behavior was reversible upon thermal cycling although again a small peak appears as a shoulder around 358 nm upon warming to room temperature. This shoulder is destroyed upon further heating. DSC

analysis of PDNOG 3 showed the presence of a broad endotherm centered at -12°C and a comparable cooling exotherm at -21°C.

Polymers with shorter alkyl chains such as poly(di-n-pentylgermane) PDNPG 2 behave somewhat different from the C₆ and C₈ derivatives. Upon cooling films of PDNPG 2 to -40°C, much smaller shifts in the maximum (338 to ~352 nm) occurred. No further changes resulted upon cooling and warming the sample regenerated the starting spectrum. DSC analysis of 2 showed a broad, very weak (1.8 cal/g *versus* 10 cal/g for PDNHG) endotherm at -23°C. Cooling revealed the related exotherm at -25°C. In this regard, it is significant to note that the spectrum of poly(di-n-pentylsilane) in the solid state was relatively insensitive to temperature and never produced an absorption at 370 nm even at temperatures as low as -80°C. Whereas the thermochromic behavior of 1 and 3 seems analogous to that observed for the related silicon polymers, the behavior of 2 is clearly somewhat different. Not only is the thermal transition very weak, but the new absorption generated at low temperatures is still 18-20 nm blue shifted from that observed for 1 and 3. At this point, it is not clear whether this shift is simply due to conformational imperfections in the backbone (e.g., gauche kinks) or to the presence of an alternative conformation(s) which absorbs at shorter wavelengths.

Related thermal and spectroscopic studies on the copolymers 4a and 4b similarly suggest that side chain crystallization and conformational locking also occurs in these materials. 4a, which contains ~23 mole % germanium, absorbs around 319 nm as a thin film. Upon cooling below 0°C, a sharp absorption appears at 362 nm and the original absorption at 318 nm decreases (see Figure 4). Warming to room temperature causes a redistribution of the intensities, but the absorption at 362 nm remains as a major

contributor. Heating the sample above 60°C regenerates the original spectrum. DSC analysis shows a broad strong endotherm peaked at 33°C and the corresponding cooling exotherm at 15°C. The germanium rich copolymer 4b (42 mole % germanium) behaved similarly except that the new peak at 362 nm mostly disappeared upon warming to room temperature. Consistently, DSC analysis showed a lower melting transition now centered around 18°C. It appears that the incorporation of increasing amounts of germanium in the silicon chain causes a progressive lowering of the side chain melting transition temperature. The fact that the position of the λ_{max} below the transition temperature of the copolymers is not identical to the corresponding homopolymers is not surprising. Even if the backbone of the copolymer were locked into an identical configuration as the respective homopolymers, there is no reason to expect that the resulting λ_{max} of a chain composed of randomly mixed silicon and germanium would absorb at exactly the same point as catenated chains of pure silicon or germanium.

As expected, the germanium homo and copolymers are quite light sensitive. Figure 5 shows the bleaching of a film of PDNHG 1 and the copolymer 4a as a function of the irradiation dose. Similarly, as reported for polysilane derivatives, the bleaching is caused by chain scission which produces lower molecular weight chain fragments. This phenomenon was verified by GPC examination of the irradiated samples.

In summary, we report the synthesis of a number of dialkyl germanium homopolymers and some copolymers with dichloro di-n-hexyl silane. Unlike the silicon derivatives, the use of diglyme as a cosolvent does not greatly improve the yields of the germanium homo and copolymers and results in the production of lower molecular weight materials. The lower molecular weight materials were spectroscopically identical to the high molecular weight samples in solution except for their UV maxima which were always

blue shifted by 8-10 nm. The positions of the λ_{\max} for the high molecular weight germanium homopolymers is red shifted by 24-27 nm relative to the respective silicon polymers in solution. In the solid state the homopolymers and copolymers are strongly thermochromic. At low temperatures, the homopolymers 1 and 3 appear to show side chain crystallization which results in a strong absorption band at ~370 nm. This band is at the same place as observed for the corresponding high molecular weight polysilane derivatives for which it has been suggested that the side chain crystallization causes conformational locking of the backbone. This suggests that the intrinsic absorption of silicon and germanium high polymers is very similar which is in accord with theoretical predictions. Similar thermochromic behavior has been observed for the copolymers although the long wavelength absorption is somewhat blue shifted from the respective germanium homopolymers.

ACKNOWLEDGMENTS

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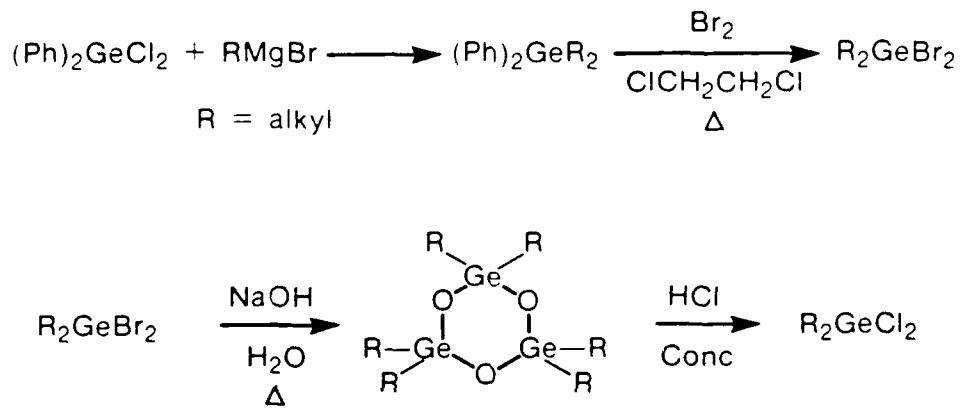
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Scheme I



Scheme II

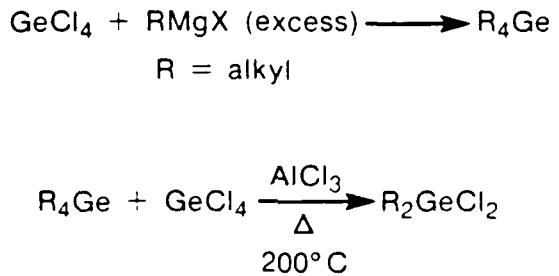
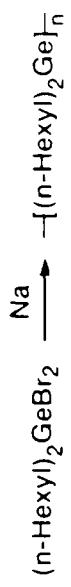


Table 1. Polymerization of dibromo-di-n-hexylgermane: (a) polymer yield before fractionation; (b) molecular weights and distributions were determined by GPC analysis using ASI ultragel columns and are relative to polystyrene standards.



Entry	Solvent	Addition Mode	% Yield ^a	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	Composition (%)
1	Toluene	Regular	23	6.64 1.32	5.35 1.27	1.24 1.04	85 15
2	Toluene	Inverse	11	5.7 1.38	4.98 1.30	1.15 1.06	74 26
3	Toluene (70) Diglyme (30)	Regular	20	7.24 1.21	5.64 1.04	1.28 1.17	46 24
4	Toluene (70) Diglyme (30)	Inverse	22	4.44 0.90	3.56 0.84	1.25 1.06	77 33

Table 2. Polymerization of dichloro-di-n-alkylgermanes: (a) crude polymer yields prior to fractionation; (b) molecular weights and distributions were determined by GPC analysis using ASI ultragel columns and are relative to polystyrene; (c) an accurate molecular weight distribution was not determined due to the small amount of high molecular weight material; (d) low molecular weight oligomers.



Entry	Monomer	Solvent	Addition Mode	% Yield ^a	$\bar{M}_w \times 10^{-3}$ ^b	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	Composition (%)
1	(C ₆ H ₁₃) ₂ GeCl ₂	Toluene	Regular	9.5	976.7 6.53 1.27	627.7 5.84 1.14	1.56 1.12 1.12	41 21 38
2	(C ₆ H ₁₃) ₂ GeCl ₂	Toluene	Inverse	5.0	986. ^c 8.29 1.59	7.4 1.18	— 1.12 1.35	<10 21 75
3	(C ₆ H ₁₃) ₂ GeCl ₂	Toluene (70) Diglyme (30)	Inverse	15.5	5.01 0.9	3.8 0.8	1.32 1.16	65 35
4	(C ₆ H ₁₃) ₂ GeCl ₂	Toluene (50) Octane (50)	Regular	9.2	985.7 6.64 1.5	594.7 5.8 1.26	1.66 1.14 1.19	50 19 32
5	(C ₅ H ₁₁) ₂ GeCl ₂	Toluene	Regular	8.3	385.12	251.9	1.53	60 40 ^d
6	(C ₈ H ₁₇) ₂ GeCl ₂	Toluene	Regular	7.0	687.9 3.4	443.7 2.3	1.55 1.48	28 72
7	(C ₆ H ₁₃) ₂ GeCl ₂ (1) (C ₆ H ₁₃) ₂ SiCl ₂ (1)	Toluene	Regular	9.0	753.9 1.30	275.6 1.23	2.74 1.05	75 25
8	(C ₆ H ₁₃) ₂ GeCl ₂ (1) (C ₆ H ₁₃) ₂ SiCl ₂ (1)	Toluene (70) Diglyme (30)	Regular	16.3	858.7 10.9 1.3	582.6 6.6 1.24	1.5 1.65 1.1	17 69 13

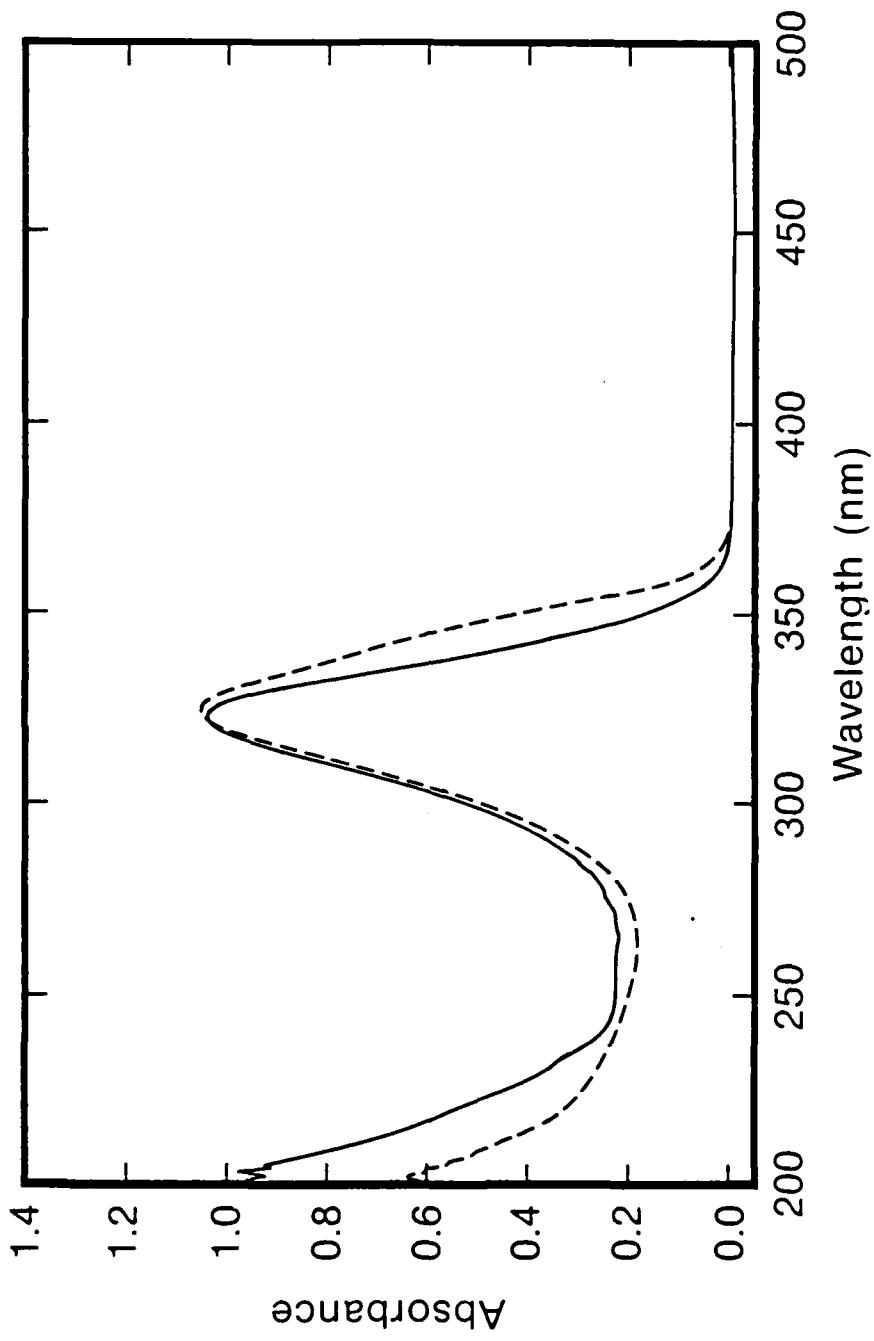


Figure 1. — copolymer 4b in cyclohexane; - - - a 1:1 mixture of poly(di-n-hexylsilane) ($\bar{M}_w = 1.6 \times 10^6$) and poly(di-n-hexylgermane) ($\bar{M}_w = 9.7 \times 10^5$) in cyclohexane.

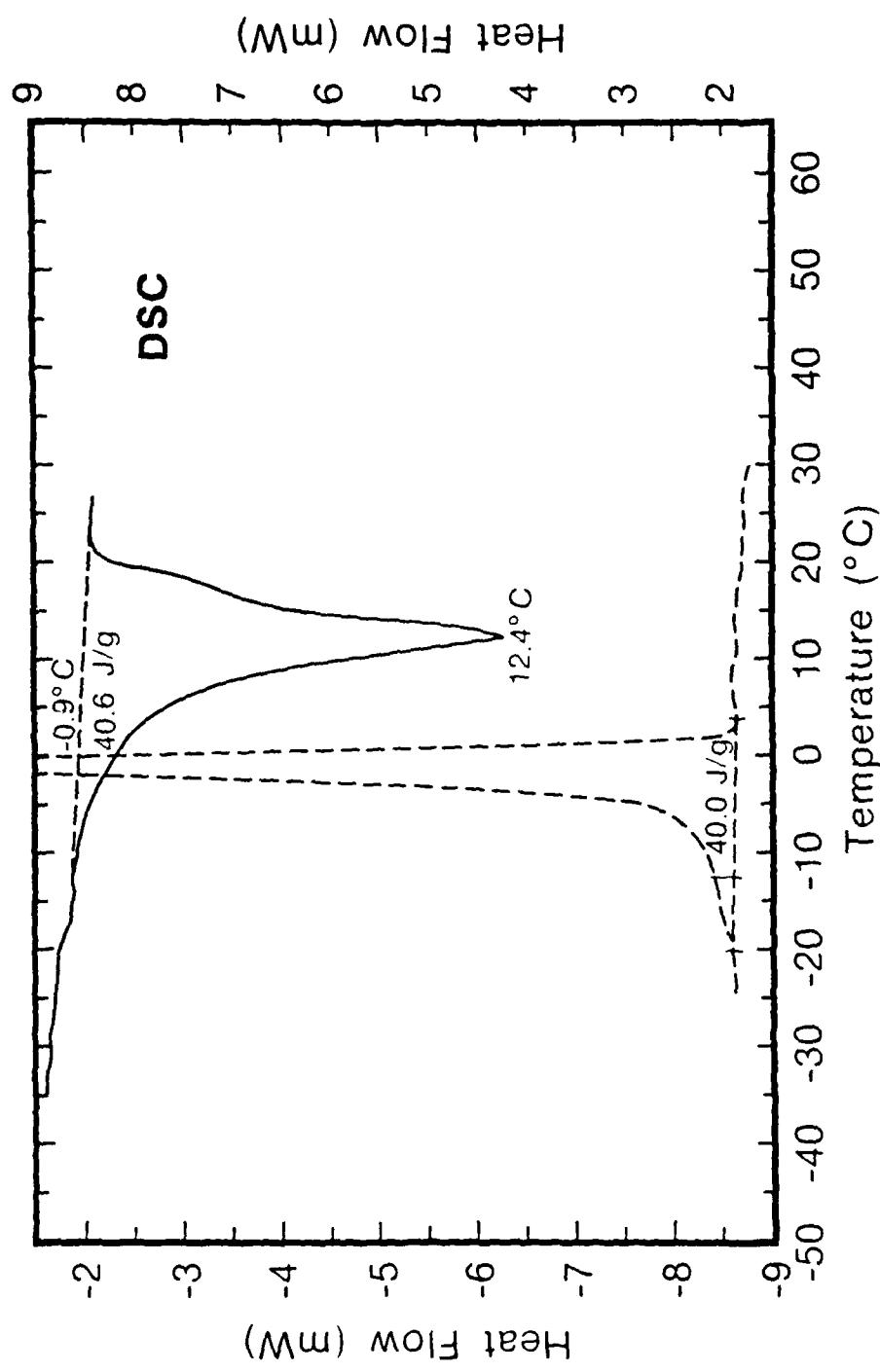


Figure 2. DSC analysis of poly(di-n-hexylgermane) (\bar{M}_w 9.7×10^5); —— heating,
 - - - cooling.

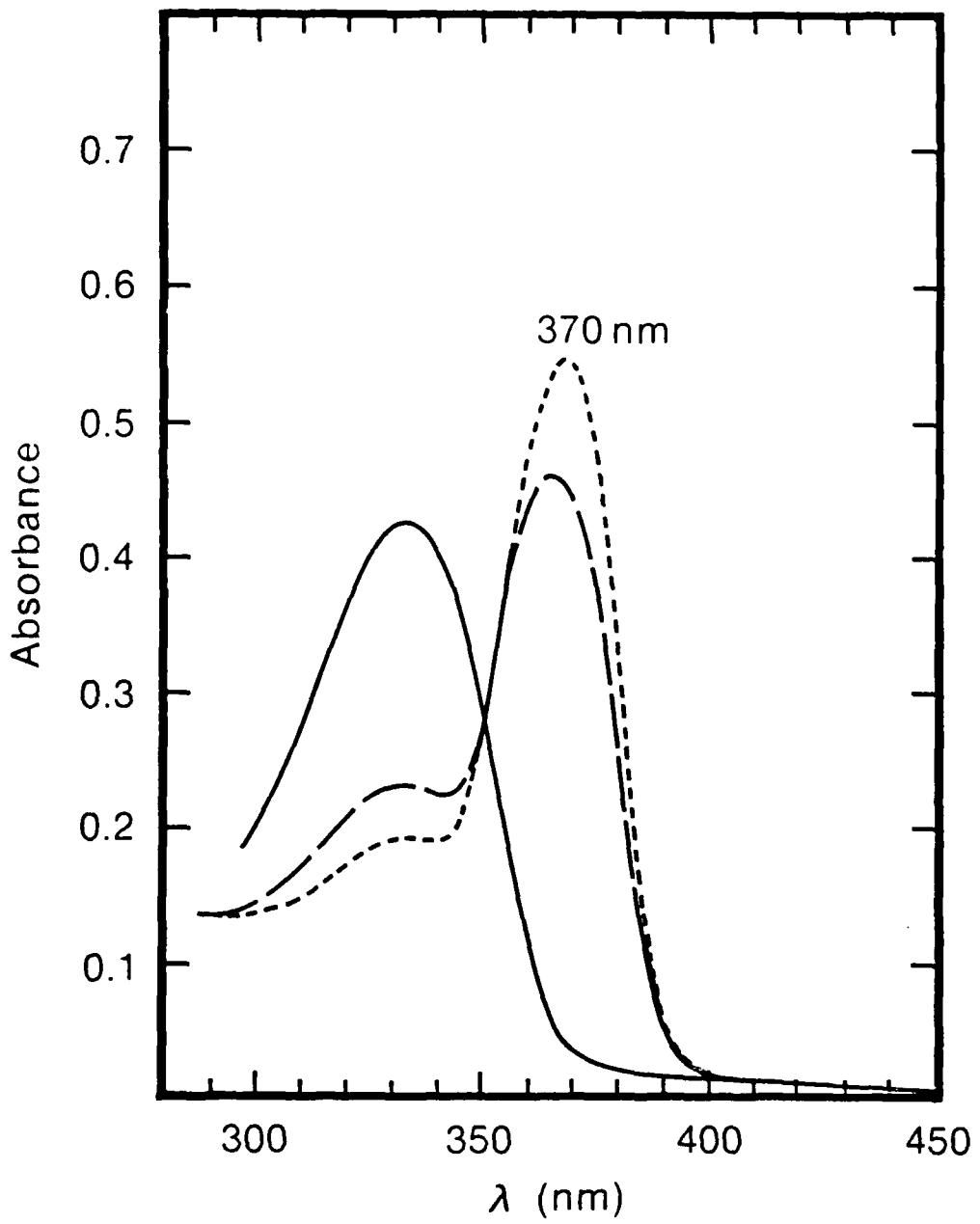


Figure 3. UV spectrum of a film of poly(di-n-hexylgermane) as a function of temperature; — 22°C, - - - -3°C, - · - - -11°C.

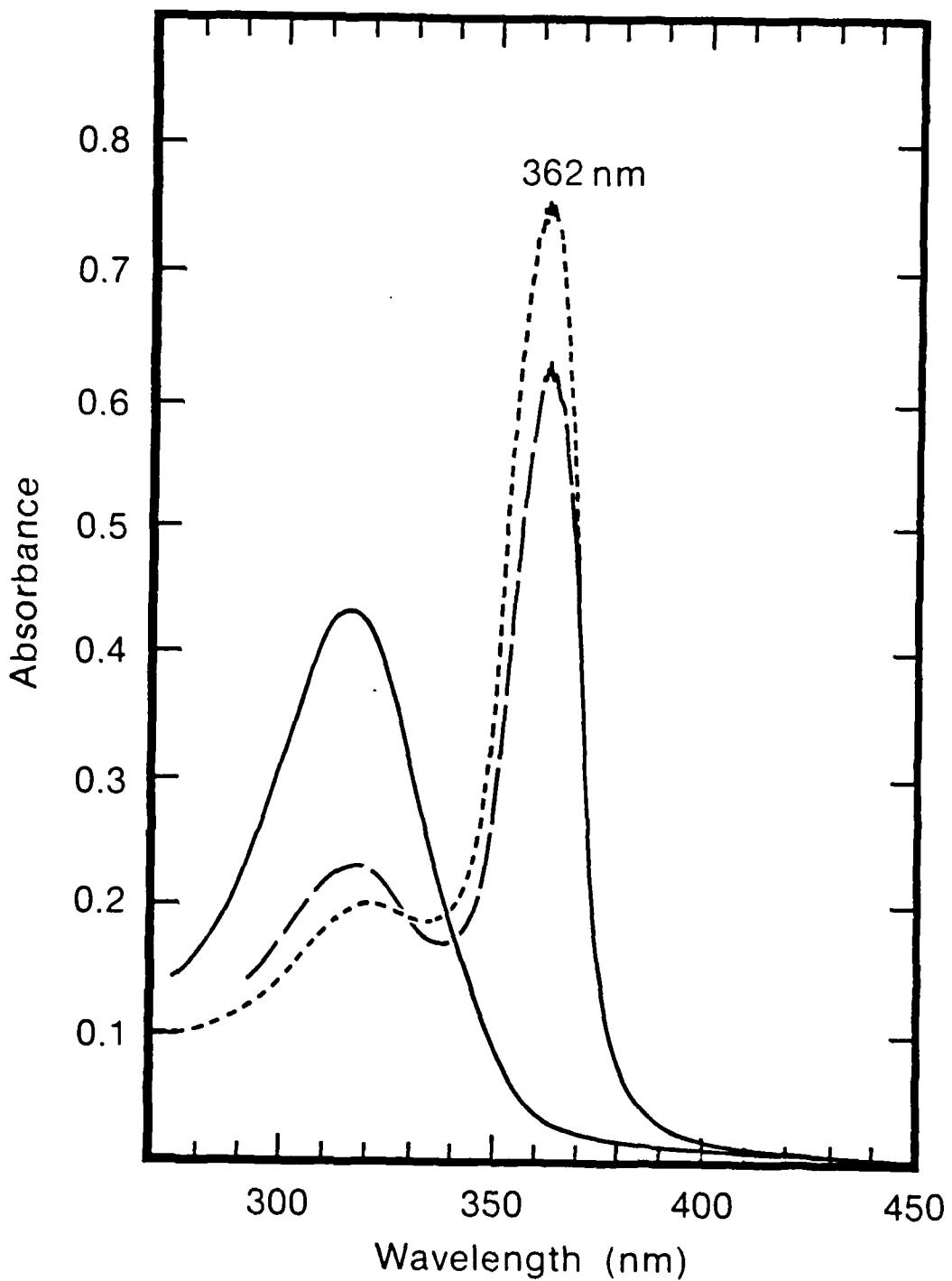


Figure 4. UV spectrum of a film of the copolymer 4a as a function of temperature:
— 22°C, - - - 0°C, - · - - -33°C.

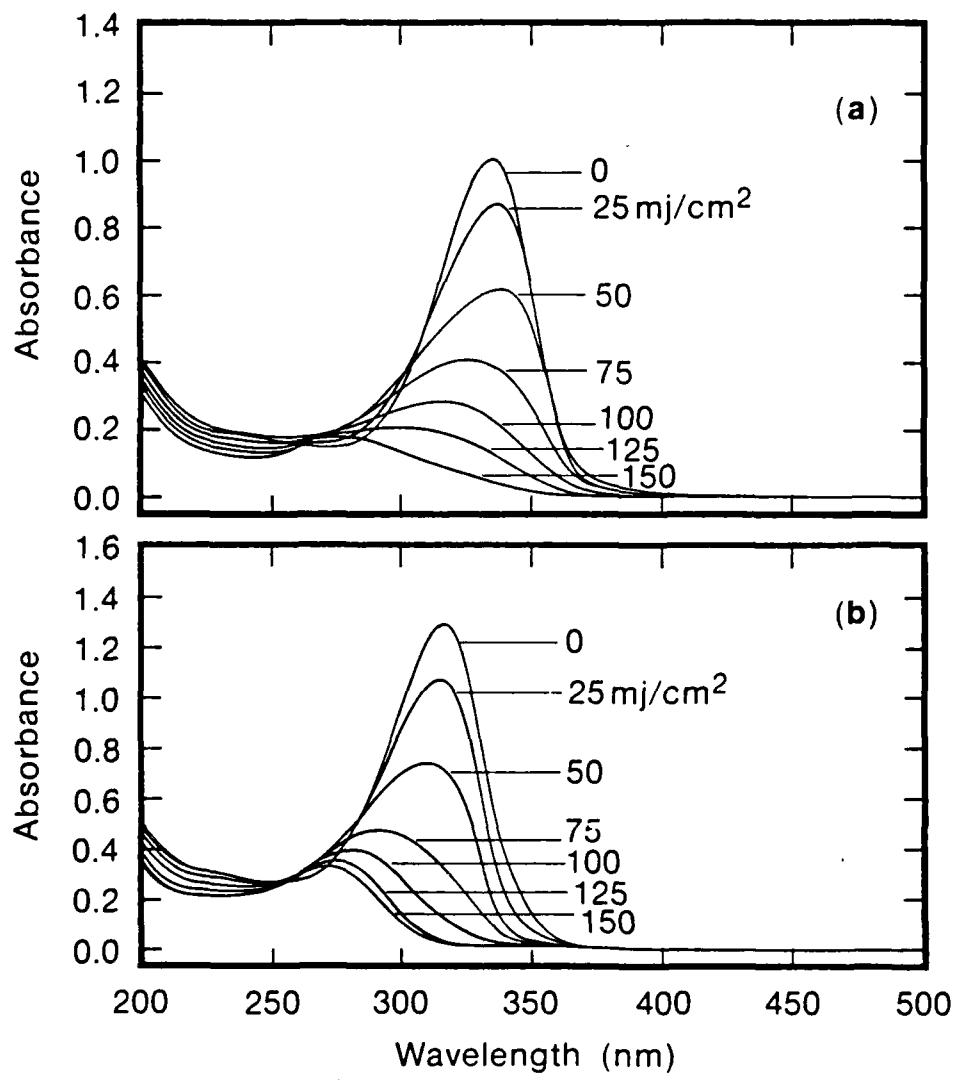


Figure 5. Bleaching of polygermane films as a function of irradiation dose:
(a) poly(di-n-hexylgermane) 1; (b) copolymer 4a.

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